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Final Report

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This work during the last three years has addressed the kinetics, dynamics, and growth of Ga, In, and As species on well-characterized silicon (100) substrates. We have studied the early stages of deposition, at a few monolayers or less. When this work was started, there was essentially no information concerning the energetics and desorption kinetics of the first prelayers of these materials on silicon, although there was strong evidence from photoemission data that As diffuses through a Ga prelayer to bind more strongly to Si.¹ During the course of this project, one other group at AT&T Bell Laboratories started to make absolute determinations of some of these parameters for Ga and As using the technique of Rutherford backscattering.²⁻⁴ In our work, we measured sticking coefficients, binding energies, and islanding behavior, and determined structures for the first several layers of Ga and In on the silicon (100) crystal. Some of our suggested structures for the growth of Ga on Si(100) have now been confirmed by scanning tunneling microscopy.⁵ We have also obtained first results for kinetic probing of As₂ dimer species and for layers of In on As-covered silicon.

Throughout the course of our work, a novel probe for detection of the gas phase species, namely laser-induced fluorescence, has been developed and used extensively, in addition to the customary tools of LEED and Auger electron spectroscopy. The laser method allows species-specific and state-specific detection, and thus we have also been able to obtain state-resolved desorption parameters in a few cases. This report describes the results of work to probe Ga, In, and As₂ species interacting with Si(100).

Apparatus

The apparatus which has been built up for these studies⁶⁻⁹ consists of a home-built molecular beam epitaxy (MBE) machine with commercial Ga, In, and As_{2,4} sources, LEED, Auger, sputter gun, and optical ports for introduction of laser beams and for collection of laser-induced fluorescence light with a photomultiplier. The apparatus operates routinely in the low 10⁻¹¹ Torr pressure range. Cryoshields are used around the MBE sources to reduce fluxes of impurities and to cut down on the scattering of species. The entire bottom section of the chamber is a titanium sublimator, which achieves an effective pumping speed of 30,000 l s⁻¹. Various species such as Ga, In, As₂, and As₄ are generated and impinge on a silicon (100) single crystal. The substrate can be heated to values over 1150 K and can be cleaned by argon ion sputtering.

The laser used in these studies is a pulsed tunable dye laser which is pumped by a XeCl excimer laser at 308 nm. The dye laser wavelengths in the visible are used to probe the resonant transitions from ²S_{1/2} to the ²P_{1/2} and ²P_{3/2} spin orbit states in Ga and In atoms by laser-induced fluorescence. The dye laser is frequency doubled in a β -barium borate crystal to obtain 240 nm light for probing individual vibrational and rotational transitions of the As₂ species on the A¹ Σ_u^+ -X¹ Σ_g^+ transition, also by laser-induced fluorescence.

We measure the scattering and sticking properties of the epitaxial species by opening and closing the beam sources and by probing the scattered fluxes at different angles with the laser. We carry out temperature programmed desorption and isothermal desorption, using the laser to probe the densities of gas phase species being desorbed in time. A unique capability of the laser detection method is the possibility of making these measurements for individual spin-orbit states, and vibrational and rotational states of the epitaxial species. With these techniques we are able to obtain the kinetic parameters which characterize the deposition and

desorption processes. The Auger electron spectrometer is used to detect the amount of impurity contamination on the surface and also to study approximate coverages of the overlayers, which gives additional information about the desorption and islanding behavior. Details about the islanding behavior are extracted from Auger peak ratios of both the overlayer and substrate and from careful analyses of the kinetic orders of the desorption at various coverages. LEED studies are used to determine the well-ordered crystalline structures of the overlayers.

Ga on Si(100) - Structures

LEED studies of the structures of Ga prelayers on Si(100) were carried out and these results were correlated to the observations for the desorption energies and the formation of islands.^{7,8} The following LEED patterns were observed for Ga overlayers on Si(100) at the stated coverages (surface temperature ≤ 350 K); similar patterns are also observed at much higher temperatures upon desorption (840 K):⁷

Si 2x1, ≤ 0.1 ML

Si:Ga 3x2, 0.15-0.35 ML

Si:Ga 5x2, 0.4 ML

Si:Ga 2x2, 0.4-0.55 ML

Si:Ga 8x1, 0.7-0.9 ML

Si:Ga 2x1, ≥ 1 ML

Similar diffraction patterns were also reported by earlier RHEED studies,¹⁰ however, no suggestions were made regarding the structures of the overlayers.

A model for the growth of Ga on Si(100) was developed in our work to account for the observed structures. This model assumes that Ga preferentially binds to silicon at the sites where there are available dangling bonds. Silicon (100) is

a reconstructed 2x1 surface; the initial square array of silicon atoms lowers its energy by joining two dangling bonds from each topmost atom to form silicon dimer rows. Scanning tunneling microscopy has confirmed the Si(100) 2x1 dimer row structure, but shows that there are typically a large number of defects as well.¹¹ In between the dimer rows, each silicon atom in the topmost layer has one available dangling bond, with which Ga can bind. Since Ga is trivalent, only two of its electrons are utilized in bonding to silicon, unless there is an unusual bonding geometry or an extraordinarily long bond. Thus, it is likely that two Ga atoms will preferentially locate near each other on the surface and dimerize.

Dimer pairs of Ga atoms form on the silicon at a coverage of 0.5 ML. This configuration is particularly stable, since all of the dangling bonds of the silicon atoms are occupied and all three electrons on the Ga atoms are bonded. Using the Ga dimer structures to fill in vacant sites on the silicon, most of the observed LEED patterns are very adequately interpreted, including the 3x2, 5x2, 2x2, and 2x1.⁷ Only preliminary suggestions for the unusual 8x1 pattern could be made.⁷ The addition of any further Ga atoms to the 2x2 structure requires removal of the Si reconstruction and an opening of the Si dimer rows, providing new sites for Ga atoms to bind. Under Ga desorption the surface reconstructs back, which decreases the surface energy; this is our tentative explanation for the observed lowering of the Ga desorption energy at coverages greater than 0.5 ML.⁸ At 1 ML, all of the topmost sites would be replaced by Ga dimer rows, lying perpendicular to the initial Si dimer rows, and the surface becomes fully passivated with Ga. Such a structure has been proposed for the As-terminated prelayer on Si(100).^{12,13}

Our suggested dimer structures for low coverages of Ga on Si(100) are qualitatively verified by scanning tunneling microscopy (STM).⁵ In addition, the STM studies find that at very low coverages the Ga dimers grow in long chains, lying in rows perpendicular to the underlying silicon dimer rows. This behavior

might be caused by a change in the free energy or a reconstruction that occurs to Si atoms bonded to Ga atoms. According to a typical electronegativity scale, Ga is 1.6 and Si is 1.8. Thus, Ga may donate electron density to Si in forming a chemical bond. The Si atom that is bound to a Ga will be relatively electron-rich, thus modifying the bonding to the adjacent Si and possibly the reconstruction, providing a preferential site for the next Ga atom to bind. At higher coverages, the long chains of Ga dimers organize into regions of 3x2, 5x2, and 2x2 order, from which we postulate the model for the growth of the overlayer.⁷ The structure of the 3x2 pattern has also been verified by STM.⁵ There have been many reports that an As prelayer on Si(100) leads to a particularly stable 2x1 dimer structure.^{12,13} Our studies of the Ga overlayers suggest that the Ga terminated surface is also stable and involves well-ordered overlayer structures.

Ga on Si(100) - Binding Energies

Our studies determined that gallium adsorbs and desorbs on silicon (100) in a reversible manner. The pattern of peaks observed in temperature programmed desorption originate from a first order desorption at coverages of less than one monolayer and from a zero order desorption at coverages above one monolayer.^{6,8,9} In addition, the sticking coefficients for Ga are found to be unity on clean silicon as well as on silicon surfaces covered with Ga. From this lack of a barrier to adsorption, we assume that the Ga binding energy is equal to its desorption energy. The Ga appears to desorb exclusively as atoms, which is reasonable since the bond energy for diatomic Ga species is small, perhaps on the order of 1 eV.¹⁴

Isothermal desorption rates are studied as a function of coverage and at different temperatures to obtain Arrhenius plots yielding the binding energy and pre-exponential factor in the first order desorption regime. Both Auger probing of the surface concentration and laser probing of the gas phase species are used in these

experiments. At coverages less than 0.5 ML, the binding energy is found to be 2.9 ± 0.2 eV,^{6,8} whereas the desorption energy decreases to 2.3 ± 0.2 for coverages between 0.5 ML and 1 ML.⁸ We have been able to understand this decrease in the binding energy from studies of the LEED structures of the Ga overlayers discussed above.⁷ At 0.5 ML, all the dangling bond sites on the Si(100) crystal are filled with Ga dimer species; additional Ga atoms must force the Si dimer rows to open, which requires energy, thus lowering the desorption energy.

Evidence for the change in desorption energy at 0.5 ML is seen from a set of Auger data which follows the isothermal desorption as a function of coverage.⁸ The log of the Ga coverage, as determined by the amplitude of the Auger signal from Ga on the surface, is determined as a function of time. A "break" in the slope occurs at 0.5 ML. The analysis of the data before and after the "break" establishes the desorption energy and pre-exponential factor for each region of coverage. A similar change in the slope may be present in the Rutherford backscattering data of Zinke-Allmang and Feldman, however, they did not analyze their data in terms of two distinct regions.² Thus, they assigned a lower desorption energy of 2.2 eV to the whole region of Ga coverage up to 1 ML. Their value of 2.2 eV may correspond to our value of 2.3 eV, which we assign only to the coverage regime of 0.5-1 ML.

For coverages above 1 ML, Ga forms three dimensional islands of Ga on top of a monolayer of Ga. The energy for desorption in this regime is found to be 2.6 ± 0.1 eV.⁸ The desorption from the islands is well characterized by zero order kinetic plots in our experiments. Our value for the desorption energy from the islands is somewhat smaller than would be expected from liquid Ga (2.9 eV), but the result is thought to be due to combined desorption from the islands and from the monolayer, which might occur at an effective lower energy.⁸

Ga on Si(100) - Islanding

When Ga impinges on a surface that has been pre-covered by one ML of Ga, there is a strong tendency to form islands on top of the well-ordered monolayer structure.⁸ This tendency was found to be very dependent on the temperature and on impurities in our studies. Data is taken with the Auger spectrometer to study the ratio of the Ga/Si peak amplitudes versus the amount of time that Ga is deposited on the surface. If Ga grows layer-by-layer, then it will obscure the Si Auger signal with increasing coverage, thus, the ratio of the two signals will increase continuously, as is the case at 300 K. Sharp breaks in the slopes of the ratios versus coverage are observed at 600 K, 380 K, and 330 K, occurring at coverages of 1 ML, 2 ML, and 2.5 ML, respectively. At 300 K, the Ga appears to grow essentially layer-by-layer (Frank-van der Merwe growth), whereas at higher temperatures a Stranski-Krastanov growth mechanism appears to occur (islands on top of a layer). A nearly horizontal slope that occurs in the 600 K data after the first monolayer suggests that the islands are three dimensional and have a high profile. Since the first sharp break at the highest temperature studied occurs at 1 ML, one monolayer of Ga on Si(100) appears to be very stable.

Islanding of Ga on Si(100) is found to be much more severe in the presence of carbon contamination. There is some evidence that islands of Ga may start to form on the bare Si substrate (Volmer-Weber growth mode).² In our studies, we observed that islands can occur on the bare Si substrate when there is C contamination.⁸ Under very clean conditions, we observe the well-ordered first layer of Ga on Si(100).

There is an important consequence of this islanding behavior for the growth of GaAs semiconductor materials on Si(100).^{15,16} The fact that Ga readily forms islands on top of either a Ga or As prelayer on Si(100)⁸ or Si(111)¹⁶ creates the undesirable morphological situation that GaAs nucleates around Ga islands on the surface. The nucleation of many tiny GaAs crystallites on Si(100) is observed in

electron micrographs.¹⁵ Annealing cycles and the use of biatomic stepped crystals of Si have had some success in removing the boundaries between the crystallites, but highest quality materials are still not achieved.

In on Si(100) - Two-Dimensional Islands

The sticking and desorption of In on Si(100) has some similarities to Ga, but there are several novel aspects, pertaining to the kinetic barriers for desorption from two and three dimensional islands. During the course of this work, a publication appeared from another group, which has also considered the desorption energies and their correlation to the structures of In on Si(100).¹⁷ While many of our results¹⁸ are found to be similar, there are several regimes that we explored which are different.

The sticking coefficients for In on Si(100) are found to be unity. For the low temperature regime (below 820 K) and at coverages ≤ 1 ML, the order of the desorption observed in our work is rigorously 1/2. This has not been observed before. At higher temperatures a first order kinetic behavior is observed, as was reported by Knall *et al.*¹⁷ The treatment of kinetic orders for desorption from two and three-dimensional solid structures is well documented.^{19,20} A half-order kinetic feature can arise when the barrier to desorption is controlled by the energy required for an atom to leave the perimeter of a two-dimensional island, move out onto the surface, and then desorb. Similarly, a desorption barrier which arises from desorption from the surface of a three dimensional island can give a 2/3 kinetic order. Such a 2/3 kinetic order is also observed in our experiments¹⁸ when we desorb multilayer coverages of In on Si(100). It appears that In has a greater propensity to coalesce into islands rather than to form well-ordered structures on Si; the desorption kinetics are controlled by this islanding behavior.

The desorption energy for In on Si(100) is measured in our studies to be

2.6 ± 0.2 eV, compared to a value of 2.8 eV, reported in Ref. 17. The heat of vaporization of In is 2.47 eV. A possible explanation for the tendency of In to form islands, in view of the rather similar energetics for vaporization from either Si or In, is likely to be found in the large lattice mismatch between In and Si. An epitaxial layer of In on Si(100) has additional strain energy, which makes it energetically more favorable to form islands of In on top of the Si.

Desorption of Spin-Orbit States

This section develops our work in state-resolved dynamics of desorption and scattering. The basic understanding of these phenomena may provide important insights for future developments in epitaxial growth. An example might be: what role does vibrational excitation play in the sticking probability of As_2 to a growing epitaxial surface? This question has never been explored before.

In a series of first studies to develop the expertise in state-resolved measurement methods, we investigated the desorption parameters to populate the two different spin-orbit states of Ga and In atoms from Si(100).^{18,21,22} There are two types of measurements that are important: the population ratios of the spin orbit states during the desorption and the desorption energy. We developed a kinetic model²¹ to describe the desorption of a two-level atom from the surface, and with this model it can be shown that the observed desorption energetics will almost always be the same for the two different spin orbit states. In fact, what is observed is always the desorption energy which is characteristic of the sum of the rates of desorption into the two channels. However, the population ratios contain information which elucidates whether or not there might be different energetic barriers to desorption for the two different states. By detailed balance, the sticking coefficients, or barriers to adsorption, contain the same information as the population ratios and are likely to be very sensitive to small differences. An

important point that comes out of the model is that if a desorption process involves the formation of several product states, a significant error can be made in the interpretation of the desorption energies if this is not recognized.

Experiments were carried out on both Ga and In to verify the consequences of the model for desorption of two-level atoms.^{18,21,22} Temperature programmed desorption curves and isothermal desorption experiments were performed with laser-induced fluorescence probing of individual $^2P_{1/2}$ and $^2P_{3/2}$ states. The results were found to be in excellent agreement with the predictions of the model. The two states appear to desorb with the same observed desorption energy, while the ratio of the observed populations is in excellent accord with the known difference in energies of the spin-orbit states, assuming that there is no preferential barrier to adsorption (or desorption) for either state. Our results suggest that the spin orbit states of either Ga or In desorb from the same "bath" of states on the surface, i.e. there are no site-specific effects which might influence the desorption of atoms from particular steps or edge sites to form one spin-orbit state or the other. The knowledge gained from the results of these measurements will be most valuable for ongoing studies of the sticking probabilities and scattering details of individual vibrational states of species such as As₂.

Laser Detection of As₂

We recently achieved laser-induced fluorescence detection of gas phase As₂ from several vibrational states, v"=0, 1, 2, 3, and 4 on the A¹Σ_u⁺-X¹Σ_g⁺ transition at ≈240 nm.²³ Laser fluorescence detection of this transition has been reported in only one other work.²⁴ In our case the molecules are excited from the desired vibrational state in the ground electronic level to the v'=5 level in the electronically excited state with a tunable laser, and then fluorescence is observed through selected interference filters to detect the state-specific density of the dimer species.

Recent spectra are taken for As_2 molecules that are scattered off a 350 K Si:As 2x1 surface. The As_2 molecules are produced by a cracker source at high temperature and undergo a collision with the surface. Only the scattered molecules are detected, since they are probed at an angle different from the incoming beam. There is no background fluorescence from ambient As_2 because of the large pumping speed in the chamber and because of the relatively low fluxes of As_2 necessary to observe excellent signals with the laser probing method.

Since the As_2 does not readily stick to the Si(100) substrate at this temperature, incomplete vibrational and rotational accommodation is observed. The rotational distribution that is measured from this spectrum is characteristic of that from the cracker source. However, significant changes in the vibrational distribution of the scattered molecules are observed for collisions with a higher temperature, 650 K, Si:As 2x1 surface. In this case, there is partial, but still incomplete vibrational accommodation, however, the $v=0$ state population is decreased distinctly in the scattered flux, and $v=2$ and 3 are enhanced. The results of these first scattering experiments give an excellent indication that state-selective scattering and sticking experiments can be performed, as will be discussed further in the section on proposed experiments below.

Comparison of Ga and As on Si(100) - Binding Energies

A fundamental difference between Ga and As with regard to the adsorption and desorption kinetics is that Ga desorbs principally as atoms, while As desorbs as As_2 dimers or As_4 tetramers. A study by Zinke-Allmang and Feldman⁴ found that the desorption energy to remove As (probably as dimers) from Si(111) is 4.3 ± 0.5 eV. They estimate from the known bond energy of As_2 (3.96 eV) that the binding energy of a single As atom to Si(111) is then ≈ 4 eV, which is considerably larger than either the 2.9 eV value obtained for Ga at low coverages or the 2.3 eV value for Ga

coverages between 0.5 and 1 ML. Their desorption studies for As on Si(111)⁴ found that As obeys second order desorption kinetics, which might be expected when two As atoms have to come together on the surface to desorb as the dimer. The desorption kinetics of both As₂ and As₄ species from GaAs are known to take on values between first and second order depending on the fluxes of the epitaxial sources.

A first experiment to determine the kinetic order for desorption of As from Si(100), using Auger spectroscopy, was carried out. We detect the change in the silicon signal as it is obscured by the coverage of As. Somewhat surprisingly we found a first order desorption. The Auger measurements are complicated by the fact that the electron beam current also affects the rate of desorption, and thus the laser-based detection method will ultimately be more reliable. However, a possible explanation for the difference in the observed kinetic orders for As on Si(100) and Si(111)⁴ (first order versus second order, respectively) may be due to the fact that on Si(100), the As forms very well-ordered dimer structures on the substrate normally. Thus if the precursor state is already a dimer, it is possible that a first order desorption will be observed from Si(100). This has been suggested to be the case in the first order desorption of As₂ and As₄ from GaAs under conditions of high fluxes of incoming As. Possibly on the Si(111) surface, the As species do not have the opportunity to form surface dimers readily because of the surface geometry, and thus the kinetics reflects the rate-limiting two-body interaction for the As atoms to form dimers during the desorption. To remove the dimer as a unit would require energy to break four well-defined Si-As bonds, and the energy required per As atom is that needed to break two As-Si bonds.

In the first experiments with the new laser detection technique for As₂ we have made preliminary measurements of the desorption of the dimers from Si(100).²³ The signal is sufficiently good that detailed temperature programmed

desorption measurements can be performed to provide a systematic study of the desorption kinetics.

In Desorption from As-Covered Si(100)

We have also obtained a first series of results to probe the influence of As prelayers on the kinetics and desorption energetics of In adlayer atoms.²⁵ Arsenic is applied to the Si(100) substrate in varying coverages, and 1 ML of indium is added on top of the prelayer and then desorbed. Indium was chosen in this first test merely because the detection system was set up for this species; however, it is planned very soon to perform similar experiments in more detail for Ga on top of As prelayers.

The As prelayer has a dramatic effect on the temperature programmed desorption curves of In. At the temperatures of interest, As₂ also will desorb, and thus the measurements are complicated by this effect. In one experiment the surface was continuously flooded with As₂ to establish a more complete coverage of arsenic. Normally, at \leq 1 ML coverages of In and without As prelayers, all of the peaks are coincident and line up near the higher temperature feature. The desorption is effectively first order for the higher temperature peak. With a prelayer of As, the In desorption features change dramatically, with In coming off at much lower temperatures. The kinetic order of the lower temperature feature is probably zero. For In on bare Si, the lower temperature peak is caused by desorption from three dimensional islands. The results suggest that In forms three dimensional islands in the presence of As much more readily than on a bare Si substrate. It is apparent that this kind of experiment, when carefully controlled, has the potential to give a tremendous amount of new information about the kinetics and energetics of heteroepitaxy.

Laser Desorption of In

One method that may be very useful to measure the surface diffusion characteristics of heteroepitaxial growth is a two-laser surface desorption/probing method.²⁶ The laser desorption method has also been used extensively to probe the concentrations of species on the surface as a function of time during a chemical process. A preliminary investigation of the potential of this method has been made in our laboratory for In overayers on Si(100). The method was modified from that used in reference 26. The 532 nm output of a frequency doubled Nd:YAG laser irradiates a small spot of In on Si(100), thermally desorbing a portion of the In in a short time. A second laser then detects the gas phase desorbed atoms after a short time delay; from this time delay information, the velocity of the desorbed atoms can be obtained. The sensitivity to In coverage in these experiments is below 10^{-3} of a monolayer. In a repetitively pulsed situation, we observe the refilling of the In atoms into the zone that is partially desorbed by the first laser by varying the time delay between desorption laser pulses. Thus measurements of surface diffusion rates can be made.

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